PERSISTENT ORGANIC POLLUTANTS IN FREE-RANGE CHICKEN EGGS IN GHANA

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Introduction

Incineration of medical waste and open burning of waste – including electronic waste – are potentially large sources of toxic chemicals known as persistent organic pollutants (POPs). These substances are slated for global reduction and elimination under the Stockholm Convention.[1] Medical waste incineration and open burning are common in developing countries and both are listed in the Stockholm Convention as source categories for unintentionally-produced POPs such as hexachlorobenzene (HCB), hexachlorobutadiene (HCBD), pentachlorobenzene (PeCB), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), and polychlorinated naphthalenes (PCNs). Municipal and electronic waste are also known to contain other chemicals listed in the Stockholm Convention such as short chain chlorinated paraffins (SCCPs), polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD).

This study investigated contamination from POPs at e-waste scrap yard and medical waste incineration sites in Ghana, focusing on POPs levels in free-range chicken eggs sampled from these sites. The free-range chicken were assumed to be "active samplers" of materials from the ground. Eggs represent an important pathway of human exposure to POPs through consumption.[2-4] To our knowledge, this is the first study to measure POPs in free-range chicken eggs from hen foraging at the Agbogbloshie e-waste scrap yard, as well as environs of incineration sites in Ghana.

Materials and methods

Free-ranged chicken eggs were sampled from e-waste scrap yard at Abgogbloshie in Accra (4 eggs), as well as from hospital incineration sites in Accra (6 eggs) and Kumasi (5 eggs) in Ghana. Poultry eggs were also sampled from supermarket in Accra (6 eggs) to serve as control. The egg samples were boiled and shipped to the laboratories based in EU countries for analyses.

All samples were analyzed for content of non-dioxin-like (indicator) PCBs (iPCBs), DDT and its metabolites, hexachlorocyclohexanes (HCHs), hexachlorobutadiene (HCBD), pentachlorobenzene (PeCB) and hexachlorobenzene (HCB) in a Czech certified laboratory (University of Chemistry and Technology in Prague, Department of Food Chemistry and Analysis). The analytes were extracted by a mixture of organic solvents hexane : dichloromethane (1:1 *v/v*). The extracts were cleaned by means of gel permeation chromatography (GPC). The identification and quantification of the analyte was conducted by gas chromatography coupled with tandem mass spectrometry detection in electron ionization mode.

The eggs were also analyzed for PBDEs and HBCD, as well as for novel BFRs (nBFRs), tetrabromobisphenol A (TBBPA) and short chain chlorinated paraffins (SCCPs) in the same laboratory as previously mentioned analyses.

Samples in this study were analyzed for PCDD/Fs and dioxin-like polychlorinated biphenyls (dl-PCBs) using the DR CALUX method. These were sent to a Dutch ISO 17025 Certified Laboratory (BioDetection Systems B.V., Amsterdam) performing the cell-based screening analysis DR CALUX according to the European Standard

EC/644/2017. Pooled egg samples were also analyzed for content of individual PCDD/Fs and an extended list of PCB congeners by HRGC-HRMS at accredited laboratory, State Veterinary Institute Prague, Czech Republic.

The free-range chicken egg samples from the Agbogbloshie scrap yard, and the control group chicken egg sample from supermarket in Accra were also analysed for polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs) in MAS Laboratory, Muenster, Germany. Accredited method MAS_PA002, ISO/IEC 17025:2005 was used to determine PBDD/Fs.

More details about sampling and analytical methods are in study published in April 2019. [6]

Results and discussion:

Organochlorine Pesticides

Sum DDT (i.e. DDT and metabolites) were relatively high in egg samples collected from the vicinity of the closed down medical waste incinerator in Accra, at a concentration of 79 ng g^{-1} (Table 1). This was however lower compared to samples from some other locations in Africa, e.g. eggs from Vikuge, Tanzania sampled in 2005 with observed level of DDT at 7041 ng g^{-1} fat.[5]

Table 1: Overview of results of chemical analyses for POPs in free-range chicken egg samples from specific locations in Ghana. Levels of POPs are in ng g^{-1} fat if not specified otherwise.

Locality	**Accra – Agbogbl.**	**Accra - hospital**	**Kumasi - hospital**	**Accra-super-market**	**EU stand./ limits**
Sample	AGB-Egg	KBI-Egg	KU-Egg	ACC-M-Egg	
Fat content (%)	14.7	12.3	14.7	8.8	
PCDD/Fs (pg TEQ g^{-1} fat)	661	49	1.74	0.39	2.50
DL PCBs (pg TEQ g^{-1} fat)	195	14.0	0.86	0.17	
Total PCDD/F + DL PCBs (pg TEQ g^{-1} fat)	856	63	2.6	0.56	5.00
PCDD/Fs DR CALUX (pg BEQ g^{-1} fat)	NA	NA	NA	NA	
Total PCDD/Fs + DL PCBs - DR CALUX (pg BEQ g^{-1} fat)	840	56	5.2	1.20	
PBDD/Fs (pg TEQ g^{-1} fat)	300	NA	NA	< 8.5	
HCB	25	3.6	0.76	< 0.2	-
PeCB	22	2.9	< 0.2	< 0.2	
HCBD	< 0.2	< 0.2	< 0.2	< 0.2	
7 PCB	286	7.8	< 1.4	< 1.4	-
6 PCB	168	7.8	< 1.2	< 1.2	40.00
PCNs *	< 1.4	NA	NA	< 1.4	-
SCCPs	2067	NA	NA	62	
sum HCH	< 0.6	< 0.6	< 0.6	< 0.6	
sum DDT	9.7	79	0.82	< 1.2	

*Seven PCN congeners were measured: PCN 52, 56, 66, 70, 73, 74 and 75.

PCDD/Fs and dl-PCBs

Two of the free-range chicken egg samples had PCDD/Fs and dl-PCBs concentrations that exceeded the EU maximum level (ML) of PCDD/Fs and sum of PCDD/Fs and dl-PCBs, expressed as WHO-TEQ.[7] The background levels for PCDD/Fs and dl-PCBs measured in chicken eggs from a supermarket in Accra were 0.39 and 0.17 pg WHO-TEQ g^{-1} fat, respectively. The highest level of dioxins (661 pg WHO-TEQ g^{-1} fat) and dl-PCBs (195 pg WHO-TEQ g^{-1} fat), were measured in eggs from Agbogbloshie scrap yard. The second highest levels of PCDD/Fs and dl-PCBs in this study, 49 and 14 WHO-TEQ g^{-1} fat respectively, were measured in eggs sampled from the area close to the closed down medical waste incinerator in Accra. There is waste incineration ash left in that area accessible to the foraging hen. Dioxin-like PCBs were lower in comparison with PCDD/Fs in most of the samples. The highest level of dl-PCB of 195 pg WHO-TEQ g^{-1} fat was measured in eggs from

Agbogbloshie. The lowest dl-PCBs in free range eggs was a sample from Kumasi – hospital site, 0.86 pg WHO-TEQ g^{-1} fat, which exceeded the background level in eggs from the supermarket by 5-fold. In Accra – hospital site, hen have access to a site with stored ash, but also forage in a larger area which is probably not contaminated with such high levels of dioxins. However, like other studies[8] have shown, incinerator fly ash with a level of dioxins (551 pg TEQ g^{-1} dw) well below the current internationally set provisional limit value for PCDD/Fs in wastes (15,000 pg TEQ g^{-1}) led to contamination of eggs at a level (49 pg TEQ g^{-1} fat) exceeding EU limit by almost 20-fold.

Hexachlorobenzene, Pentachlorobenzene and Hexachlorobutadiene

Among the free-range egg samples in this study, the highest levels of PeCB and HCB were measured in eggs from Agbogbloshie. None of the samples was above LOQ for HCBD. The highest level of HCB observed in this study in Agbogbloshie (25 ng g^{-1} fat) is consistent with levels found in Kwamrefu, Tanzania with a mean value of HCB (23 ng g^{-1} fat).[9]

Non-dioxin-like PCBs

Levels of 6 or 7 indicator PCB congeners represent a potential influence of technical mixtures of PCBs, which is likely not the outcome of unintentional generation, but intentional production and use. The EU limit for 6 i-PCB congeners in eggs is set at 40 ng g^{-1} fat. The egg samples from Agbogbloshie were more than 4-times this limit value for i-PCBs. The reason might be that technical PCBs were present in oils from car wrecks and WEEE which ended up at the scrap yard.

PBDD/Fs and BFRs

In the egg samples from Agbogbloshie, high levels of PBDEs and HBCD were also measured (1258 and 1961 ng g^{-1} fat, respectively). The level of PBDEs is comparable to e-waste dismantling sites studied by Labunska et al. in Eastern China.[10] The level of HBCD in eggs from Agbogbloshie is one of the highest ever measured, comparable to very high levels measured in Germany (2000 ng g^{-1} fat).[11] However, in eggs from Shetpe in Kazakhstan the level of HBCD in samples was one order of magnitude higher than that measured in samples from Agbogbloshie. It was speculated that the source of contamination of eggs in Shetpe were chicken feeding among car wrecks and ingesting particles of brominated materials from deteriorated car interiors that had entered the soil.[12,13] This exposure pathway is somewhat similar for the eggs from Agbogbloshie. Another potential source of contamination might also be a polystyrene foam used in obsolete electronic devices or in their packaging.[14]

Short Chain Chlorinated Paraffins (SCCPs)

Egg samples from Agbogbloshie and Accra supermarkets, were, to our knowledge, the first egg samples from Africa which have been analyzed for SCCPs. Measured levels in these samples were 2067 and 62 ng g^{-1} fat in eggs from Agbogbloshie and Accra – supermarket, respectively. By way of comparison, the EU limits of SCCPs in water is 0.4 ng g^{-1}.[15] The total concentrations of SCCPs in eggs ranged from 477 to 111,000 ng g^{-1} fat from an e-waste- polluted area in South China.[16] Level of SCCPs in eggs from Agbogbloshie (2067 ng g^{-1} fat) was higher than the minimum level but it was also much lower than maximum level from the South China site.

Conclusion

Eggs sampled at the Agbogbloshie scrap yard in Ghana contained the highest level of brominated dioxins ever measured in eggs and one of the highest ever measured levels of the flame retardant chemical, HBCD. These eggs also contained the second highest level of chlorinated dioxins ever measured in eggs. [6] An adult eating just one egg from a free-range chicken foraging in Agbogbloshie area would exceed the European Food Safety Authority (EFSA) tolerable daily intake (TDI) for chlorinated dioxins as it was set in 2018[17] by 220-fold. Indicator PCBs in these eggs were four-fold higher than the EU standard [7] and dioxins and dioxin-like PCBs were 171-fold higher than the standard. These eggs also contained very high levels of SCCPs and PBDEs and relatively high levels of other POPs such as PeCB and HCB. These findings raise further concerns about e-waste 'recycling' at Agbogbloshie and add further information to already published results of high levels of POPs measured in soil, sediments, water and human tissues. Dioxins and dioxin-like PCBs have previously been found in high levels in egg samples from Egypt, Senegal, Kenya and Tanzania connected to pollution hot spots in Africa, mostly related to waste.[18] This underscores the findings of this current study and highlights the need to improve waste management and to control dioxin flow in wastes, including the need for stricter limit values for POPs in wastes (e.g. Low POPs Content).

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